

PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Polyesters

We, COURTAULDS LIMITED, a British Company of 18, Hanover Square, London, W.1., (formerly of 16 St. Martin's-le-Grand, in the City of London), England, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

According to the present invention a polyester comprises residues of a polybasic carboxylic acid or carbonic acid and an isohexide.

Isohexides are the 1, 4—3, 6 dianhydrides of mannitol, sorbitol and iditol and are obtainable by the acid-catalysed dehydration and cyclisation of the parent hexitols or of the intermediate 1, 4 or 3, 6 hexitans. The three isohexides are known as isomannide, isosorbide and isoidide after their respective parent polyols.

The polyester may be made by condensing the isohexide with the polybasic acid or a latent polybasic acid, for example a polyacid halide, including phosgene, a polyacid anhydride, or a polyester. The conditions of the polyesterification may be varied in known manner according to the constitution of the acid component. For example, when a polybasic acid is condensed with an isohexide, the temperature of the reaction is necessarily greater than when the acid is in the form of its chloride. There are, however, a number of catalysts which enable the polyesterification reaction to proceed at lower temperature and the catalysed reaction produces a polyester of better colour. Stannous phosphide, antimony trifluoride, antimony trioxide and litharge are examples of such catalysts.

The polyesters may be derived from dibasic acids or acids of greater functionality. Linear polyesters are formed when dibasic acids alone are condensed with an isohexide with or without another glycol being pre-

sent. Some of the linear polyesters are fibre-forming materials, and have a latent ability to cross-link in the opening of the cyclic ether components of the isohexide structure. For example, the condensation of a dibasic acid chloride with an isohexide in anhydrous conditions and with no acid-acceptor present, can result in a cross-linked structure. The hydrochloric acid evolved during the condensation is an active agent for opening a cyclic ether group, thereby generating an alcohol group and rendering the isohexide unit into a triol which forms a cross-linked polyester with a dibasic acid.

A particularly valuable class of polyesters according to this invention is the poly(isohexide carbonate) formed by reacting the isohexide with phosgene with the elimination of HCl or with a carbonate ester, for example, diphenyl carbonate, with the elimination of an alcohol, for example phenol from diphenyl carbonate. We have obtained poly(isosorbide carbonate) having a melting point of 203°C. from the ester interchange reaction. This value is well above the known melting points of other polycarbonates derived from aliphatic alcohols. For example in Volume 1 of "High Polymers" published by Interscience Publishers, at Page 31, there is a table of properties and melting points of aliphatic polycarbonates including poly(trimethylene carbonate) which is an unstable glass, poly(tetramethylene carbonate) a powder melting at 59°C., poly(pentamethylene carbonate) melting at 44° to 46°C., poly(hexamethylene carbonate) melting at 55° to 60°C. and one derived from a diol containing an ether group, as does an isohexide, namely poly(diethylene carbonate), which is liquid at room temperatures.

The value of the isohexides as replacements for other glycols, in particular ethylene glycol, in the manufacture of linear, fibre-forming polyesters, is that some of the polymers, for example poly(isohexide iso-

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- phthalate) may be dry-spun from such volatile solvents as methylene chloride to form filaments of good quality. The polymers based on ethylene glycol are not sufficiently soluble in common volatile solvents for this to be practicable. 25
- In the finished state, the polyester filaments containing an isohexide have a higher water imbibition than those made from an analogous polymer in which the isohexide is replaced by ethylene glycol. Perhaps as a result of this property, or the fibre structure which gives rise to it, the isohexide polyester filaments also show increased affinity for both slowly and rapidly diffusing disperse dyes. 30
- The invention is illustrated by the following Examples in which parts are by weight:—
- EXAMPLE 1. 35
- A mixture of 194 parts of dimethyl terephthalate, 146 parts of isosorbide and 2 parts of litharge was heated in a tube immersed in a vapour bath whilst a slow stream of nitrogen was passed through the mixture. The bath had an initial temperature of 202°C. which was maintained for 4½ hours before being raised to and held at 222°C. for 1½ hours. In the final stage of the polyesterification reaction the temperature was raised to 283°C. and maintained for 1 hour during which time the pressure in the tube was reduced to 1 mm. Hg. 40
- The cooled product was a dark brittle glass having an inherent viscosity of 0.23 dl/gm. at 0.5 *per cent* concentration in meta-cresol at 25°C. Birefringent fibres could be pulled from the melt, the birefringence being lost on heating the product to 175°C. and complete melting occurring at 196°C. 45
- EXAMPLE 2.
- A number of other polyesters were made by the ester-interchange method employed in Example 1. The details are recorded in the following Table I in which the acidic component, a diester, and isohexide are identified, together with the conditions of the reaction, and the properties of the products.

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TABLE I

Reaction conditions						Product			
Diester	Isohexide	Molar proportions	Maximum temperature	Total Duration	Catalyst	Description	*I.V.(d/g)	Softening point	Melting point
diethyl malonate	isosorbide	1:1	202°C. @ 1 mm. Hg.	4 hours	Ca(OAc) ₂ + Sb ₂ O ₃	Brittle, brown glass; fibre-forming	0.065		52°C.
diethyl succinate	isosorbide	1:1	222°C. @ 1 mm. Hg.	4 hours	Ca(OAc) ₂ + Sb ₂ O ₃	Highly viscous dark brown oil	0.040		25°C.
diethyl adipate	isosorbide	1:1	283°C. @ 1 mm. Hg.	4 hours	Ca(OAc) ₂ + Sb ₂ O ₃	Highly viscous dark brown oil	0.067		25°C.
dimethyl terephthalate	isosorbide	1:1	283°C. @ 1 mm. Hg.	4 hours	SbF ₃	Brittle glass; Fibre-forming	0.229	175°C.	196°C.

*The I.V. determinations on the polyesters were made at 0.5 per cent concentration in *m*-cresol at 25°C.

EXAMPLE 3.

A charge of 183 parts of adipyl chloride and 146 parts of isosorbide was placed in a vessel equipped with a stirrer, thermometer, a gas inlet for nitrogen and a gas outlet. The flask was heated gently with the stirrer rotating and copious fumes of hydrogen chloride were evolved at between 35°C. and 40°C. The fumes were swept from the vessel by a stream of nitrogen admitted to the vessel immediately below the surface of the charge. The temperature was raised to 90°C. after 1 hour and then to 200°C. over the course of 2 hours at the end of which time the vessel was briefly evacuated to remove HCl gas. The product when cooled was a tough, transparent mass which was incompletely soluble in methylene chloride. The insoluble

portion was separated by filtration and the filtrate poured into methanol. A gummy precipitate was obtained which dried to a horny mass under vacuum. The dried precipitate had an inherent viscosity of 0.79 dl/g at 0.1 per cent concentration in meta-cresol at 25°C.

EXAMPLE 4.

Other polyesters were made by reacting diacid chlorides with isohexides according to the procedure followed in Example 3. The properties of the polyesters and the reaction conditions employed are recorded in the following Table II, which identifies the diacid chloride, isohexide and those reaction conditions which vary in detail from the previous Example.

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TABLE II

Reaction conditions					Product			
Diacid chloride	Isohexide	Molar proportions	Maximum temperature	Duration at max. temperature	Description	I.V. (dl/g)	Softening point	Melting point
dimethyl galactaryl chloride	isosorbide	1:1	180°C.	1 hour	Brittle glass	0.128	153°C.	156°C.
sebacoyl chloride	isosorbide	1:1	95°C.	1 hour	Rubbery	0.425	—	63—82°C.
terephthalyl-chloride	isosorbide	1:1	220°C.	1 hour	Transparent glass; fibre forming	0.172	165°C.	185°C.

EXAMPLE 5.

5 A mixture of 146 parts of isosorbide and 214 parts of diphenyl carbonate was heated in a glass tube immersed in a vapour bath at 222°C. whilst a slow stream of nitrogen was passed through the mixture. Phenol distilled off readily without the help of a catalyst to promote the ester interchange. After 10 15 minutes, the pressure was reduced to 1 mm. Hg. for 30 minutes and the contents of the tube were cooled at the end of this period. The product was dissolved in an acidified methylene chloride/ethanol mixture (9 volumes to 1 volume) and poured into an excess of methanol from which it was re- 15 gained as a brownish-white polymeric powder.

20 The polymer had an inherent viscosity of 0.35 dl/g at 0.5 per cent concentration in meta-cresol at 25°C. and birefringent fibres could be drawn from the melt. The fibres

lost their birefringence at 185°C. to 190°C. and melted at 203°C.

EXAMPLE 6.

25 A solution of 73 parts of isosorbide and 102.5 parts of isophthaloyl chloride in 480 parts of nitrobenzene were placed in a glass reaction vessel which was partially immersed in a vapour bath at 222°C. and a slow stream of nitrogen was passed through the solution. Hydrogen chloride was evolved rapidly at first but after 20 minutes the reaction had 30 slowed and the rate of passage of nitrogen was then increased. The reaction was allowed to continue for a total of 6 hours during which time the viscosity of the solution increased. The solution was cooled, diluted with methylene chloride and poured into a large excess of methanol, when poly(isosor- 35 bide isophthalate) was precipitated. The polymer had an inherent viscosity of 40

0.66 dl/g. A fibre drawn from the polymer melt was found to lose its birefringence at 190°C. and to melt at 211°C. Multifilament yarn could be produced by extruding the polymer through an electrically heated strip jet. The yarn could be cold drawn to give a tenacity of 2.8 g/denier and 57 per cent extension.

EXAMPLE 7.

A poly(isosorbide isophthalate) prepared substantially as in Example 6 had an inherent viscosity of 0.56 dl/g. A fibre drawn from the polymer melt lost its birefringence at 195°C. and melted at 216°C. The polymer was melt spun to give multi-filament yarn and after stretching at 150°C. had a tenacity of 1.9 g/denier and 54 per cent extension. The stretched yarn was shown to have an increased affinity for both slow and rapidly diffusing disperse dyes compared with a polyethylene terephthalate yarn. The water imbibition of the poly(isosorbide isophthalate) yarn was found to be 5.5 per cent compared with 3.5 per cent for a polyethylene terephthalate yarn.

EXAMPLE 8.

A poly(isosorbide isophthalate) prepared by the method described in Example 6 had an inherent viscosity of 0.53 dl/g and a melt drawn fibre lost birefringence at 175°C. to 180°C. and melted at 215°C. The polymer was soluble in a number of common solvents including methylene chloride and chloroform though in many cases the polymer would begin to precipitate in spherulitic form after an interval of some days. The polymer could be successfully dry-spun from freshly prepared solutions and multi-filament yarn so obtained from a methylene chloride solution, after stretching both in steam and in the

cold, gave a tenacity of 2.1 g/denier and 47 per cent extension.

EXAMPLE 9.

A mixture of 73 parts of isosorbide, 101.5 parts of terephthaloyl chloride and 480 parts of nitrobenzene was heated in a flask equipped with a reflux condenser and nitrogen inlet at the lowest point. As the temperature approached 160°C., hydrogen chloride was evolved rapidly. Heating was continued until the nitrobenzene refluxed gently and a constant flow of nitrogen was maintained to remove the acidic gas. Refluxing was continued for 5 hours during which time the solution had become increasingly viscous. It was then cooled, diluted with methylene chloride and the poly(isosorbide terephthalate) precipitated by pouring the solution into a large excess of methanol.

The polyester had an inherent viscosity of 0.57 dl/g and fibres could be drawn from the polymer melt. These fibres could be cold drawn and melted at 230°C. to 235°C.

WHAT WE CLAIM IS:—

1. Polyesters incorporating isohexide residues.
2. Linear polyesters incorporating isohexide residues.
3. Poly(isohexide carbonate).
4. Poly(isohexide isophthalate).
5. Polyesters as claimed in any preceding claim in which the isohexide is isosorbide.
6. Fibres of polyesters according to any preceding claim.
7. Fibres made by a process substantially as described with reference to the Examples.

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